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**(54) DEEP DESULFURIZATION CATALYST, METHOD FOR PREPARING THE SAME AND METHOD  
FOR DESULFURIZATION USING THE SAME**

(57) A catalyst for deep desulfurization of a mineral oil corresponding to kerosene, comprising a nickel component of nickel and nickel oxide, zinc oxide, and aluminum oxide, wherein the content of the nickel component in terms of nickel oxide is from 5 to 25% by weight and the content of the zinc oxide is from 30 to 70% by weight each based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide, the nitrogen monoxide adsorption of the catalyst at 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa) and 40°C after hydrogen reduction at 360°C is 4.0 ml/g or more in terms of standard-state, and the catalyst has a specific surface area of from 10 to 300 m<sup>2</sup>/g; the deep desulfurization catalyst, which is obtained by carrying out an activation treatment in the presence of hydrogen at a temperature of from 200 to 400°C and a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup>

to 1.96 MPa); a process for producing the deep desulfurization catalyst, comprising mixing a basic substance with each of an aqueous solution of a water-soluble nickel metal salt and an aqueous solution of a water-soluble zinc metal salt or with a mixed aqueous solution thereof to thereby form precipitates separately or simultaneously, and mixing the precipitates with aluminum oxide or an aluminum oxide precursor, followed by molding and burning; and a method of deep desulfurization, comprising bringing a mineral oil corresponding to kerosene into contact with hydrogen in the presence of the above deep desulfurization catalyst at a temperature of from 200 to 400°C, a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa), and an LHSV (liquid hourly space velocity) of from 0.1 to 5.

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**Description****TECHNICAL FIELD**

5 [0001] The present invention relates to a catalyst for deep desulfurization of a mineral oil corresponding to kerosene, a production process thereof, and a deep desulfurization method using the catalyst. More particularly, the present invention relates to a deep desulfurization catalyst usable for deep desulfurization conducted as a step of pretreating a mineral oil which corresponds to kerosene and is to be subjected to steam reforming reaction, and to a production process thereof and a deep desulfurization method using the catalyst.

**BACKGROUND ART**

10 [0002] Processes for hydrogen production include water electrolysis, which has been known from long ago, and techniques proposed recently, such as the partial oxidation of light hydrocarbons and autothermal reforming (ATR). However, a steam reforming process is suitable for small hydrogen generators and fuel cell systems because it is a relatively inexpensive process for hydrogen production excellent in handleability.

15 [0003] Since steam reforming catalysts are generally apt to be poisoned by sulfur compounds, it is necessary to desulfurize (pretreat) feedstock hydrocarbons beforehand. Because of this, hydrocarbons having a low sulfur content or lighter-than-naphtha hydrocarbons, which are readily desulfurized, have been mainly used so far. However, since 20 hydrocarbons such as naphthas are not on general market, use thereof has a problem concerning availability to small consumers possessing small hydrogen production apparatus or possessing hydrogen generation apparatus for fuel cell systems. Furthermore, it is said that such hydrocarbons have a problem concerning handleability because of their high volatility, etc.

25 [0004] Recently, clean energies are increasingly expected from the standpoint of environmental preservation, and there is a desire for a technique for producing hydrogen from a raw fuel excellent in availability, handleability, and profitability. Although desulfurization to several hundred ppb or lower is required because steam reforming catalysts are readily poisoned, it is exceedingly difficult to deeply desulfurize mineral oils corresponding to kerosene because they contain aromatic sulfur compounds, i.e., so-called non-desulfurizable compounds. In particular, some small hydrogen production apparatus and fuel cell systems have no hydrogen purification unit because apparatus miniaturization is indispensable thereto. It is therefore necessary to design a catalyst on the supposition of cases where the hydrogen to be used for desulfurization contains carbon dioxide, etc. In the case of using hydrogen in which carbon dioxide is present, there is the higher possibility of posing problems, for example, that temperature control becomes difficult due to heat of reaction because the methanation reaction of these proceeds besides desulfurization reaction.

30 [0005] Furthermore, even when a mineral oil corresponding to kerosene can be desulfurized to a several hundred ppb level with a conventional catalyst under such operation conditions as to give an elevated degree of desulfurization, then this process has problems of the possibility of kerosene alteration (yellowing, etc.), catalyst powdering, hydrogen sulfide leakage to the downstream side, high reaction pressure, etc. Under these circumstances, it is desired to develop a desulfurization catalyst having even higher performance while taking account of simplification of apparatus constitution and long-term stable operation.

**DISCLOSURE OF THE INVENTION**

40 [0006] An object of the present invention is to provide a deep desulfurization catalyst having such activity and strength that a mineral oil corresponding to kerosene can be deeply desulfurized to 0.1 wt. ppm (= 100 wt. ppb) or lower under relatively low-pressure conditions even with hydrogen containing carbonic acid gas while inhibiting methanation reaction and preventing oil alteration and that long-term stable operation is possible, a process for producing the catalyst, and a method of deep desulfurization using the same.

45 [0007] The present invention relates to a catalyst for deep desulfurization of a mineral oil corresponding to kerosene, comprising a nickel component of nickel and nickel oxide, zinc oxide, and aluminum oxide, wherein the content of the nickel component in terms of nickel oxide is from 5 to 25% by weight and the content of the zinc oxide is from 30 to 70% by weight each based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide,

50 the nitrogen monoxide adsorption of the catalyst at 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa) and 40°C after hydrogen reduction at 360°C is 4.0 ml/g or more in terms of standard-state, and the catalyst has a specific surface area of from 10 to 300 m<sup>2</sup>/g.

55 [0008] Furthermore, the present invention relates to the above deep desulfurization catalyst, which is obtained by

carrying out an activation treatment in the presence of hydrogen at a temperature of from 200 to 400°C and a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa).

5 [0009] Moreover, the present invention relates to a process for producing the above deep desulfurization catalyst, comprising mixing a basic substance with each of an aqueous solution of a water-soluble nickel metal salt and an aqueous solution of a water-soluble zinc metal salt or with a mixed aqueous solution thereof to thereby form precipitates separately or simultaneously, and mixing the precipitates with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

10 [0010] Also, the present invention relates to a method of deep desulfurization, comprising bringing a mineral oil corresponding to kerosene into contact with hydrogen in the presence of the above deep desulfurization catalyst at a temperature of from 200 to 400°C, a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa), and an LHSV (liquid hourly space velocity) of from 0.1 to 5.

#### BEST MODE FOR CARRYING OUT THE INVENTION

15 [0011] The present invention will be explained below in detail.

[0012] The present inventors made intensive investigations in order to accomplish the above objects. As a result, they have found that a mineral oil corresponding to kerosene can be deeply desulfurized to a sulfur content of 0.1 ppm or lower by using a catalyst which is obtained through the step of subjecting a water-soluble nickel metal salt and a water-soluble zinc metal salt as raw materials to precipitation from a base solution, the step of mixing the precipitates 20 with aluminum oxide or an aluminum oxide precursor, and a burning step and which comprises nickel or nickel oxide, zinc oxide, and aluminum oxide in specific amounts, has a specific nitrogen monoxide adsorption at ordinary pressure and 40°C after hydrogen reduction at 360°C, and has a specific surface area in a specific range. The present invention has thus been completed.

25 Catalyst Composition:

[0013] The deep desulfurization catalyst of the present invention comprises three components, i.e., a nickel component of nickel and nickel oxide, zinc oxide, and aluminum oxide.

[0014] The content of the nickel component in terms of nickel oxide is from 5 to 25% by weight, preferably from 5 to 30% by weight, and especially preferably from 10 to 18% by weight, based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide. The nickel component serves to react the sulfur compounds contained in a mineral oil corresponding to kerosene (hereinafter, this mineral oil is referred to as "kerosene") with hydrogen to convert them into hydrogen sulfide. When the content thereof is 5% by weight or higher, preferred desulfurization performance is obtained. When the content thereof is 25% by weight or lower, the nickel component has a higher degree of dispersion to enable the catalytic performance to be sufficiently exhibited. The proportion of nickel to nickel oxide in the nickel component is not particularly limited.

[0015] The content of the zinc oxide is from 30 to 70% by weight, preferably from 40 to 70% by weight, and especially preferably from 50 to 70% by weight, based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide. The zinc oxide serves to properly maintain an oxidized state of the nickel and to trap hydrogen sulfide being generated. Consequently, when the content thereof is 30% by weight or higher, these performances can be sufficiently exhibited and methanation is inhibited to thereby sufficiently inhibit hydrogen sulfide leakage. When the content thereof is 70% by weight or lower, the nickel component and the aluminum component which will be described below are present in appropriate amounts to enable the catalytic performance to be sufficiently exhibited.

[0016] Aluminum oxide functions not only to increase the specific surface area to thereby facilitate the contact of the catalyst (active sites) with a kerosene and hydrogen (improve the catalyst effectiveness factor) but also to maintain strength. The content of the aluminum oxide is preferably from 5 to 65% by weight, more preferably from 10 to 65% by weight, and most preferably from 20 to 50% by weight, based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide. By regulating the content thereof to 5% by weight or higher, sufficient strength and a sufficient catalyst effectiveness factor are obtained. When the content thereof is 65% by weight or lower, the nickel component and zinc oxide are present in appropriate amounts to enable the catalyst performance to be sufficiently exhibited.

[0017] The deep desulfurization catalyst of the present invention, after hydrogen reduction in which from 50 to 500 mg of the catalyst is held at 360°C for 2 hours while passing hydrogen therethrough, has a nitrogen monoxide adsorption at 40°C of 4 ml/g or more, preferably from 4.0 to 7.0 ml/g, and especially preferably from 5.0 to 6.7 ml/g, in terms of standard-state (standard temperature and pressure: stp) adsorption. By regulating the nitrogen monoxide adsorption to 4 ml/g or more, sufficient desulfurization activity can be obtained. The nitrogen monoxide adsorption may be regarded as a measure of the amount of active sites of the desulfurization catalyst. It is reasonable to select carbon monoxide

as a probe (probe molecule) for catalysts which function in a metallic state. However, for catalysts in which the oxidized state is difficult to specify like the catalyst of the present invention, it is more practical to select nitrogen monoxide, which is adsorbable even to active sites having a relatively highly oxidized state, as a probe (e.g., Suzuki, Yoshizawa, *et al.*, *Journal of the Japan Institute of Energy*, Vol. 74, p. 806 (1995)).

5 [0018] The specific surface area is from 10 to 300 m<sup>2</sup>/g, more preferably from 30 to 250 m<sup>2</sup>/g, and most preferably from 40 to 200 m<sup>2</sup>/g. The specific surface area is measured by the BET method and expressed as a BET specific surface area (Braunauer-Ermmett-Tailor specific surface area).

10 Methods of Catalyst Preparation:

[0019] Various methods such as the impregnation method, precipitation method, coprecipitation method, kneading method and the like can be used for catalyst preparation. However, the precipitation method and coprecipitation method are most preferred because the catalyst of the present invention produced by these methods is apt to sufficiently exhibit its performance.

15 [0020] Preferred examples of catalyst preparation methods include a process for producing the deep desulfurization catalyst described above which comprises mixing a basic substance with each of an aqueous solution of a water-soluble nickel metal salt and an aqueous solution of a water-soluble zinc metal salt or with a mixed aqueous solution of both to thereby form precipitates separately or simultaneously, and mixing the precipitates with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

20 [0021] An embodiment of the preferred catalyst preparation method comprises preparing, for example, a mixed aqueous solution of a water-soluble zinc salt and a water-soluble nickel salt, dropping thereinto an alkaline water as a basic substance, sufficiently evenly mixing the resultant precipitate, and mixing this precipitate with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

25 [0022] Alternatively, the method may be a method which comprises dropping an alkaline water as a basic substance into each of an aqueous solution of a water-soluble zinc salt and an aqueous solution of a water-soluble nickel salt, sufficiently evenly mixing the resultant precipitates, and mixing the precipitate mixture with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

30 [0023] When compositions equal to the nickel precipitate and zinc precipitate are available, the same performance is obtained also by sufficiently mixing these compositions with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

35 [0024] Examples of the water-soluble nickel salt include easily available water-soluble nickel salts, such as nickel nitrate, nickel chloride, nickel acetate and the like. Examples of the water-soluble zinc salt include inorganic zinc, such as zinc nitrate, zinc borate, zinc chloride, zinc acetate and the like, and organic zinc. As the aluminum oxide,  $\gamma$ -alumina is most preferred. The specific surface area of the aluminum oxide is preferably from 100 to 350 m<sup>2</sup>/g, more preferably from 150 to 300 m<sup>2</sup>/g, and most preferably from 180 to 250 m<sup>2</sup>/g. With respect to the particle size, aluminum oxide powder which passes through a 100-mesh screen is preferred and one which passes through a 150-mesh screen is more preferred. Aluminum oxide powder which passes through a 180- to 200-mesh screen is easiest to handle.

40 [0025] The aluminum oxide precursor may be one which becomes aluminum oxide upon burning. Examples thereof include aluminum hydroxide, aluminum isopropoxide, and the like. Incidentally, aluminum isopropoxide can be converted to aluminum oxide by dissolving it in a solvent, e.g., ethylene glycol, hydrolyzing and condensation-polymerizing the aluminum isopropoxide using an acid or base as a catalyst, and then burning the reaction product (alkoxide method).

45 [0026] Aluminum hydroxide can be preferably used as the aluminum oxide precursor. With respect to the particle size, aluminum hydroxide powder which passes through a 100-mesh screen is preferred and one which passes through a 150-mesh screen is more preferred. Aluminum hydroxide powder which passes through a 180- to 200-mesh screen is easiest to handle.

50 [0027] For molding, a known method can be preferably selected, such as extruding, punching, press molding or the like. A shape suitable for the reactor and operation conditions can be selected, such as a cylindrical shape, Raschig ring, hollow shape, spherical shape or the like. For punching, an organic substance or inorganic compound can be added as a binder.

55 [0028] Examples of the basic substance include chlorides, sulfates, carbonates, and similar compounds of alkali metals or alkaline earth metals, ammonia, organic amines, and the like. Preferred are basic carbonates such as ammonium carbonate, sodium carbonate, and calcium carbonate and ammonia. More preferred are ammonium carbonate and ammonia. A combination of ammonium carbonate and ammonia is especially preferred. When ammonium carbonate and ammonia are used in combination, they are used in a proportion in the range of preferably from 1:9 to 9:1, especially preferably from 2:8 to 8:2.

[0029] The basic substance may be added as it is to the aqueous solution of a water-soluble nickel metal salt and that of a water-soluble zinc metal salt or to the mixed aqueous solution of these. Alternatively, the basic substance may be added in the form of an aqueous solution. However, it is preferred to add the basic substance in the form of

an aqueous solution.

[0030] The precipitates are preferably dried before being mixed with aluminum oxide or an aluminum oxide precursor. Methods for drying are not particularly limited, and various drying methods are applicable. Although the drying temperature also is not particularly limited, it is preferably from 80 to 140°C. The drying time is preferably from 1 to 24 hours.

[0031] The burning temperature is preferably from 320 to 520°C, more preferably from 320 to 400°C, and most preferably from 350 to 400°C. By regulating the burning temperature to 320°C or higher, sufficient strength is obtained. By regulating the burning temperature to 520°C or lower, adverse influences such as sintering are diminished. Although the burning time is not particularly limited, 0.1 to 24 hours may be usually sufficient.

10 Method of Desulfurization:

[0032] The catalyst of the present invention is packed into a fixed-bed reactor, which is operated at a temperature of from 200 to 400°C, preferably from 220 to 350°C, and most preferably from 240 to 330°C; an LHSV of from 0.1 to 5 vol/vol h<sup>-1</sup>, preferably from 0.5 to 4 vol/vol h<sup>-1</sup>, and more preferably from 0.5 to 3 vol/vol h<sup>-1</sup>; and a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa), preferably from 1 to 15 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.47 MPa), and more preferably from 1 to 10 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 9.80×10<sup>-1</sup> MPa). The hydrogen/kerosene volume ratio is from 30 to 300, preferably from 40 to 200, and most preferably from 50 to 150, in terms of standard-state ratio.

[0033] By desulfurizing a kerosene under the conditions described above, deep desulfurization to 0.1 ppm or lower can be attained without causing alteration.

[0034] Even when the hydrogen contains carbonic acid gas, the mineral oil corresponding to kerosene can be desulfurized. The allowable concentration of carbonic acid gas is 30 vol% or lower, preferably 25 vol% or lower, and more preferably 15 vol% or lower. By regulating the content of carbonic acid gas to a value within this range, the partial hydrogen pressure is prevented from decreasing relatively and a high degree of desulfurization is obtained.

[0035] The deeply desulfurized kerosene actually obtained with the catalyst and desulfurization method of the present invention is colorless and transparent.

[0036] By regulating the reaction temperature to 200°C or higher, desired desulfurization performance is obtained. By regulating the reaction temperature to 400°C or lower, kerosene alteration and the formation of by-products can be inhibited. There are no particular limitations on the lower limit of LHSV. However, LHSV's of 0.1 vol/vol h<sup>-1</sup> and higher are preferred from the standpoint of profitability because an increased efficiency of desulfurization per unit time is attained. By using an LHSV of 5 vol/vol h<sup>-1</sup> or lower, high desulfurization performance is obtained. With respect to pressure, there are no particular limitations on the upper limit. However, the practical upper limit is 20 kg/cm<sup>2</sup> (1.96 MPa) from the standpoints of the cost of construction and production, etc. Furthermore, by using a pressure of 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa) or higher, the partial hydrogen pressure is prevented from decreasing and desired desulfurization performance can be exhibited. By regulating the hydrogen/kerosene volume ratio to 30 or higher, the amount of the oil passed per unit time is not limited. By regulating the ratio to 300 or lower, the hydrogen reacts sufficiently and the size of the apparatus can be reduced.

[0037] Although the catalyst of the present invention exhibits given performances when placed in a hydrogen atmosphere, it is preferable to perform a reduction treatment before the desulfurization treatment. By conducting a reduction treatment beforehand, stable catalytic activity can be obtained from the initial stage of a desulfurization reaction. A reduction treatment is preferred because the time required for the activity to reach a stationary region can be shortened as a result of the reduction treatment. Conditions for the activation treatment (hydrogen reduction treatment) include a temperature of from 200 to 400°C, preferably from 300 to 400°C, and most preferably from 330 to 380°C. When the temperature is 200°C or higher, it is preferable because sufficient activation is attained. The temperature is 380°C or lower, it is preferable because catalyst sintering and methanation induced by excessive reduction are diminished. The pressure is from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa), preferably from 1 to 15 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.47 MPa), and most preferably from 1 to 10 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 9.80×10<sup>-1</sup> MPa). Usually, the same pressure as in the desulfurization is satisfactory. The amount of hydrogen to be passed is not particularly limited, and the treatment may be conducted at a suitable GHSV (gas hourly space velocity) in the range of from 100 to 9,000 vol/vol h<sup>-1</sup>. Although the reduction time varies depending on catalyst amount, reactor shape, etc. and is not determined unconditionally, it may be from 1 to 24 hours.

[0038] Mineral oils corresponding to kerosene which can be deeply desulfurized with the catalyst of the present invention are not particularly limited as long as they are mineral oils corresponding to kerosene. However, properties of the mineral oils corresponding to kerosene include a flash point of preferably 40°C or lower, a 95% running temperature, among distillation characteristics, of preferably 270°C or lower, a sulfur content of preferably 0.008% by weight or lower, and an aromatic content of preferably 20 vol% or lower.

[0039] The present invention will be described in more detail and explained concretely by means of Examples, but the scope of the present invention should not be construed as being limited by the Examples.

[0040] Procedures for instrumental analyses of properties, etc. are summarized below prior to the Examples.

## Measurement of Nitrogen Monoxide Adsorption:

[0041] An automatic gas adsorption apparatus (Type R6015) manufactured by Okura Riken was used for the measurement of nitrogen monoxide adsorption. A 50 to 500 mg portion of a sample was precisely weighed out and placed in a U-shaped sample tube made of quartz or borosilicate glass (commonly called "Pyrex glass"). High-purity helium was passed therethrough to purge away the air. Thereafter, the sample was heated from room temperature to 360°C over about 1 hour while passing hydrogen. After the temperature had reached 360°C, the sample was held for 2 hours in a hydrogen stream and then cooled to 40°C over 1 to 2 hours while passing high-purity helium gas again. A given amount (0.1 ml) of high-purity nitrogen monoxide (produced by Takachiho Kagaku; research grade) was passed over the sample at that temperature, and the amount of the nitrogen monoxide remaining unadsorbed was determined with a thermal conductivity detector (TCD). From the adsorption at 40°C was calculated the adsorption in the standard state (STP).

## Measurement of Specific Surface Area of Catalyst:

[0042] A surface area-measuring apparatus (Belsorp 28SA) manufactured by Bell Japan Corp. was used for the measurement of BET specific surface area. A 500 to 1,000 mg portion of a sample was precisely weighed out and packed into a sample tube made of quartz. The sample was heated from room temperature to 300°C over 1 hour while evacuating the tube to a vacuum on the order of from  $10^{-1}$  to  $10^{-3}$  mmHg, and was held at that temperature for 2 hours under reduced pressure to conduct a degassing treatment. Thereafter, the sample was cooled to room temperature with evacuation, and the atmosphere in the tube was replaced with high-purity helium gas. The sample thus degassed was precisely weighed. Thereafter, the sample was allowed to adsorb nitrogen at a liquefied-nitrogen temperature (-196°C) to measure the specific surface area thereof.

## Sulfur Content Determination:

[0043] The sulfur content of a product was determined by the Raney nickel method (minimum limit of detection, 0.1 wt. ppm). For ascertaining the leakage of hydrogen sulfide to the downstream side, a Kitagawa's detector tube (minimum limit, 0.1 wt. ppm) was used.

## EXAMPLE 1

[0044] In 1,200 ml of ion-exchanged water were dissolved 5.8 g of nickel nitrate hexahydrate and 24.3 g of zinc acetate dihydrate. To this solution were added 10 wt% ammonium carbonate and 15 wt% ammonia water. Thus, a precipitate of zinc and nickel compounds was obtained. This precipitate was taken out by filtration, washed with water, and then dried at 120°C for 12 hours. To the precipitate obtained was added 19.5 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 510°C for 24 hours to obtain Catalyst A containing 5 wt% nickel oxide, 30 wt% zinc oxide, and 65 wt% aluminum oxide. Catalyst A had a specific surface area of 248 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 4.0 ml/g. Ten grams of Catalyst A was precisely weighed out and reduced with hydrogen at a temperature of 400°C and a pressure of 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa) for 3 hours. Subsequently, a commercial white kerosene (manufactured by Cosmo Oil Co., Ltd.; JIS #1 kerosene; sulfur content, 50 wt. ppm) was passed therethrough at a temperature of 400°C, a pressure of 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa), and an LHSV of 0.1 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 300. For the desulfurization was used hydrogen containing 15 vol% carbonic acid gas. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed and almost no methane generated. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 2

[0045] In 1,200 ml of ion-exchanged water were dissolved 10.0 g of nickel acetate tetra hydrate and 43.9 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 15 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst B containing 10 wt% nickel oxide, 40 wt% zinc oxide, and 50 wt% aluminum oxide. Catalyst B had a specific surface area of 225 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 4.8 ml/g. Ten grams of Catalyst B was precisely weighed out and reduced with hydrogen at a temperature of 380°C and a pressure

of 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 350°C, a pressure of 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa), and an LHSV of 0.5 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 200. For the desulfurization was used hydrogen containing 20 vol% carbonic acid gas. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed and almost no methane generated. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 3

[0046] In 1,200 ml of ion-exchanged water were dissolved 17.5 g of nickel nitrate hexahydrate and 65.8 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 11.5 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 370°C for 24 hours to obtain Catalyst C containing 15 wt% nickel oxide, 60 wt% zinc oxide, and 25 wt% aluminum oxide. Catalyst C had a specific surface area of 188 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 5.8 ml/g. Ten grams of Catalyst C was precisely weighed out and reduced with hydrogen at a temperature of 360°C and a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 330°C, a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa), and an LHSV of 2 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 150. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 4

[0047] In 1,200 ml of ion-exchanged water were dissolved 21.0 g of nickel nitrate hexahydrate and 18.0 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 6.6 g of  $\gamma$ -aluminum powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 330°C for 24 hours to obtain Catalyst D containing 18 wt% nickel oxide, 60 wt% zinc oxide, and 22 wt% aluminum oxide. Catalyst D had a specific surface area of 183 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 6.3 ml/g. Ten grams of Catalyst D was precisely weighed out and reduced with hydrogen at a temperature of 360°C and a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 330°C, a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa), and an LHSV of 2.5 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 100. For the desulfurization was used hydrogen containing 25 vol% carbonic acid gas. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed and almost no methane generated. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 5

[0048] In 1,200 ml of ion-exchanged water were dissolved 15.0 g of nickel acetate tetra hydrate and 54.8 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 16.1 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 350°C for 24 hours to obtain Catalyst E containing 15 wt% nickel oxide, 50 wt% zinc oxide, and 35 wt% aluminum oxide. Catalyst E had a specific surface area of 203 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 6.1 ml/g. Ten grams of Catalyst E was precisely weighed out and reduced with hydrogen at a temperature of 330°C and a pressure of 15 kg/cm<sup>2</sup> (1.47 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 240°C, a pressure of 15 kg/cm<sup>2</sup> (1.47 MPa), and an LHSV of 3.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 100. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 6

[0049] In 1,200 ml of ion-exchanged water were dissolved 20.0 g of nickel acetate tetra hydrate and 56.6 g of zinc acetate dihydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 4.6 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst F containing 20 wt% nickel oxide, 70 wt% zinc oxide, and 10 wt% aluminum oxide. Catalyst F had a specific surface area of 165 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 6.7 ml/g. Ten grams of Catalyst F was precisely weighed out and reduced with hydrogen at a temperature of 300°C and a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 220°C, a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa), and an LHSV of 4.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 40. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## EXAMPLE 7

[0050] In 1,200 ml of ion-exchanged water were dissolved 24.9 g of nickel acetate tetra hydrate and 56.6 g of zinc acetate dihydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 1.5 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst G containing 25 wt% nickel oxide, 70 wt% zinc oxide, and 5 wt% aluminum oxide. Catalyst G had a specific surface area of 158 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 6.9 ml/g. Ten grams of Catalyst G was precisely weighed out and reduced with hydrogen at a temperature of 200°C and a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 200°C, a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa), and an LHSV of 5.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 50. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

Table 1

Example	1	2	3	4	5	6	7
Catalyst Composition							
Content in terms of nickel oxide (wt%)	5	10	15	18	15	20	25
Zinc oxide (wt%)	30	40	60	60	50	70	70
Aluminum oxide (wt%)	65	50	25	22	35	10	5
Catalyst Pretreatment							
Reduction temperature (°C)	400	380	360	360	330	300	200
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	1 (9.80 $\times$ 10 <sup>-2</sup> )	10 (9.80 $\times$ 10 <sup>-1</sup> )	8 (7.84 $\times$ 10 <sup>-1</sup> )	8 (7.84 $\times$ 10 <sup>-1</sup> )	15 (1.47)	20 (1.96)	20 (1.96)
Desulfurization Conditions							
Temperature (°C)	400	350	330	330	240	220	200
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	1 (9.80 $\times$ 10 <sup>-2</sup> )	10 (9.80 $\times$ 10 <sup>-1</sup> )	8 (7.84 $\times$ 10 <sup>-1</sup> )	8 (7.84 $\times$ 10 <sup>-1</sup> )	15 (1.47)	20 (1.96)	20 (1.96)
LHSV (vol/vol h <sup>-1</sup> )	0.1	0.5	2	2.5	3	4	5
Hydrogen/kerosene (vol/vol)	300	200	150	100	100	40	50

Table 1 (continued)

Example	1	2	3	4	5	6	7
Desulfurization Conditions							
Carbonic acid gas content (vol%)	15	20	0	25	0	0	0
Methanation	no	no	-	no	-	-	-
Catalyst Properties							
Specific surface area (m <sup>2</sup> /g)	248	225	188	183	203	165	158
NO adsorption (ml/g (stp) at 40°C	4	4.8	5.8	6.3	6.1	6.7	6.9
Cracking of catalyst after reaction	no						
Properties of Desulfurized Kerosene							
Sulfur content (wt. ppm)	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1
Hydrogen sulfide leakage	no						
Color of deeply sulfurized kerosene	*	*	*	*	*	*	*

\*: Colorless transparent

## COMPARATIVE EXAMPLE 1

[0051] In 1,200 ml of ion-exchanged water were dissolved 3.5 g of nickel nitrate hexahydrate and 56.6 g of zinc acetate dihydrate. To this solution were added 10 wt% ammonium carbonate and 15 wt% ammonia water. Thus, a precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1. This precipitate was taken out by filtration, washed with water, and then dried at 120°C for 12 hours. To the precipitate obtained was added 8.1 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 510°C for 24 hours to obtain Catalyst a containing 3 wt% nickel oxide, 70 wt% zinc oxide, and 27 wt% aluminum oxide. The catalyst a had a specific surface area of 191 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 3.3 ml/g. Ten grams of Catalyst a was precisely weighed out and reduced with hydrogen at a temperature of 400°C and a pressure of 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa) for 3 hours. Subsequently, a commercial white kerosene (manufactured by Cosmo Oil Co., Ltd.; sulfur content, 50 wt. ppm) was passed therethrough at a temperature of 400°C, a pressure of 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa), and an LHSV of 0.1 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 300. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.8 wt. ppm and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## COMPARATIVE EXAMPLE 2

[0052] In 1,200 ml of ion-exchanged water were dissolved 20 g of nickel acetate tetra hydrate and 87.7 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. This precipitate was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst b containing 20 wt% nickel oxide and 80 wt% zinc oxide. Catalyst b had a specific surface area of 10 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 3.8 ml/g. Ten grams of Catalyst b was precisely weighed out and reduced with hydrogen at a temperature of 380°C and a pressure of 10 kg/cm<sup>2</sup> (9.80×10<sup>-1</sup> MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 350°C, a pressure of 10 kg/cm<sup>2</sup> (9.80×10<sup>-1</sup> MPa), and an LHSV of 0.5 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 200. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.2 wt. ppm or lower and this deeply desulfurized kerosene

was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, cracks and slight powdering were observed.

5 COMPARATIVE EXAMPLE 3

[0053] In 1,200 ml of ion-exchanged water were dissolved 17.5 g of nickel nitrate hexahydrate and 27.4 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 27.5 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 370°C for 24 hours to obtain Catalyst c containing 15 wt% nickel oxide, 25 wt% zinc oxide, and 60 wt% aluminum oxide. Catalyst c had a specific surface area of 240 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 4.5 ml/g. Ten grams of Catalyst c was precisely weighed out and reduced with hydrogen at a temperature of 360°C and a pressure of 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 330°C, a pressure of 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa), and an LHSV of 2.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 150. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. However, during the desulfurization reaction, leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

20 COMPARATIVE EXAMPLE 4

[0054] In 1,200 ml of ion-exchanged water were dissolved 40.9 g of nickel nitrate hexahydrate and 40.5 g of zinc acetate dihydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 27.5 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 370°C for 24 hours to obtain Catalyst d containing 35 wt% nickel oxide, 50 wt% zinc oxide, and 15 wt% aluminum oxide. Catalyst d had a specific surface area of 173 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 3.7 ml/g. Ten grams of Catalyst d was precisely weighed out and reduced with hydrogen at a temperature of 330°C and a pressure of 15 kg/cm<sup>2</sup> (1.47 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 240°C, a pressure of 15 kg/cm<sup>2</sup> (1.47 MPa), and an LHSV of 3.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 100. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.2 wt. ppm and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

35 COMPARATIVE EXAMPLE 5

[0055] In 1,200 ml of ion-exchanged water were dissolved 5.0 g of nickel acetate tetra hydrate and 21.9 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 22.5 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst e containing 5 wt% nickel oxide, 20 wt% zinc oxide, and 75 wt% aluminum oxide. Catalyst e had a specific surface area of 263 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 5.0 ml/g. Ten grams of Catalyst e was precisely weighed out and reduced with hydrogen at a temperature of 300°C and a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 220°C, a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa), and an LHSV of 4.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 50. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene was colorless and transparent. However, during the desulfurization reaction, leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

50 COMPARATIVE EXAMPLE 6

[0056] In 1,200 ml of ion-exchanged water were dissolved 17.5 g of nickel nitrate hexahydrate and 27.4 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 18.0 g of  $\gamma$ -alumina powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 370°C

for 24 hours to obtain Catalyst f containing 15 wt% nickel oxide, 25 wt% zinc oxide, and 60 wt% aluminum oxide. Catalyst f had a specific surface area of 240 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 5.8 ml/g. Ten grams of Catalyst f was precisely weighed out and reduced with hydrogen at a temperature of 360°C and a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 480°C, a pressure of 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa), and an LHSV of 2.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 150. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.1 wt. ppm or lower and this deeply desulfurized kerosene had yellowed. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

10

## COMPARATIVE EXAMPLE 7

[0057] In 1,200 ml of ion-exchanged water were dissolved 15.0 g of nickel acetate tetra hydrate and 27.4 g of zinc nitrate hexahydrate. A precipitate of zinc and nickel compounds was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 27.5 g of aluminum hydroxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 370°C for 24 hours to obtain catalyst g containing 15 wt% nickel oxide, 25 wt% zinc oxide, and 60 wt% aluminum oxide. Catalyst g had a specific surface area of 240 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 5.8 ml/g. Ten grams of Catalyst g was precisely weighed out and reduced with hydrogen at a temperature of 360°C and a pressure of 20 kg/cm<sup>2</sup> (1.96 MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 150°C, a pressure of 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa), and an LHSV of 2.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 150. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.6 wt. ppm and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, no leakage of hydrogen sulfide to the downstream side was observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

## COMPARATIVE EXAMPLE 8

[0058] In 1,200 ml of ion-exchanged water was dissolved 20 g of nickel acetate tetra hydrate. A precipitate of a nickel compound was obtained in the same manner as in Example 1 and then dried. To the precipitate obtained was added 24 g of aluminum oxide powder. This mixture was sufficiently kneaded, subsequently molded with an extruder into a columnar shape having an outer diameter of 1.6 mm, and burned at 400°C for 24 hours to obtain Catalyst h containing 20 wt% nickel oxide and 80 wt% aluminum oxide. Catalyst h had a specific surface area of 270 m<sup>2</sup>/g and a nitrogen monoxide adsorption at 40°C (STP) of 5.9 ml/g. Ten grams of Catalyst h was precisely weighed out and reduced with hydrogen at a temperature of 380°C and a pressure of 10 kg/cm<sup>2</sup> (9.80×10<sup>-1</sup> MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 350°C, a pressure of 10 kg/cm<sup>2</sup> (9.80×10<sup>-1</sup> MPa), and an LHSV of 0.5 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) was regulated to 200. For the desulfurization was used hydrogen containing 25 vol% carbonic acid gas. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 0.9 wt. ppm and this deeply desulfurized kerosene was colorless and transparent. During the desulfurization reaction, leakage of hydrogen sulfide to the downstream side was observed and methane generation was also observed. After completion of the reaction, the catalyst was taken out and, as a result, no cracks were observed.

Table 2

Comparative Example	1	2	3	4	5	6	7	8
Catalyst Composition								
Content in terms of nickel oxide (wt%)	3	20	15	35	5	15	15	20
Zinc oxide (wt%)	70	80	25	50	20	25	25	0
Aluminum oxide (wt%)	27	0	60	15	75	60	60	80

Table 2 (continued)

Comparative Example	1	2	3	4	5	6	7	8
Catalyst Pretreatment								
Reduction temperature (°C)	400	380	360	330	300	360	360	380
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	1 (9.80 × 10 <sup>-2</sup> )	10 (9.80 × 10 <sup>-1</sup> )	8 (7.84 × 10 <sup>-1</sup> )	15 (1.47)	20 (1.96)	20 (1.96)	20 (1.96)	10 (9.80 × 10 <sup>-1</sup> )
Desulfurization Conditions								
Temperature (°C)	400	350	330	240	220	480	150	350
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	1 (9.80 × 10 <sup>-2</sup> )	10 (9.80 × 10 <sup>-1</sup> )	8 (7.84 × 10 <sup>-1</sup> )	15 (1.47)	20 (1.96)	8 (7.84 × 10 <sup>-2</sup> )	8 (7.84 × 10 <sup>-2</sup> )	10 (9.80 × 10 <sup>-2</sup> )
LHSV(vol/vol h <sup>-1</sup> )	0.1	0.5	2	3	4	2	2	0.5
Hydrogen/kerosene (vol/vol)	300	200	150	100	50	150	150	200
Carbonic acid gas content (vol%)		25						25
Methanation		no						present
Catalyst Properties								
Specific surface area (m <sup>2</sup> /g)	191	10	240	173	263	240	240	270
NO adsorption (ml/g (stp) at 40°C)	3.3	3.8	4.5	3.7	5	5.8	5.8	5.8
Cracking of catalyst after reaction	no	present	no	no	no	no	no	no
Properties of Desulfurized Kerosene								
Sulfur content (wt. ppm)	0.8	0.2	≤0.1	0.2	≤0.1	≤0.1	0.6	0.9
Hydrogen sulfide leakage	no	no	present	no	present	no	no	present
Color of deeply	*	*	*	*	*	yel-	*	*

\* Colorless transparent

Table 2 (continued)

Comparative Example	1	2	3	4	5	6	7	8
Properties of Desulfurized Kerosene								
sulfurized kerosene						lowed		

## REFERENCE EXAMPLE 1

[0059] Ten milliliters of a commercial desulfurization catalyst was reduced with hydrogen at a temperature of 360°C and a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa) for 3 hours. Subsequently, the commercial white kerosene was passed therethrough at a temperature of 330°C, a pressure of 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa), and an LHSV of 2.0 vol/vol h<sup>-1</sup>. The hydrogen/kerosene ratio (vol/vol at STP) in this operation was regulated to 150. After 500-hour reaction, the deeply desulfurized kerosene had a sulfur content of 1 wt. ppm and this deeply desulfurized kerosene had yellowed. Furthermore, during the desulfurization reaction, leakage of hydrogen sulfide to the downstream side was observed.

Table 3

Reference Example	1
Commercial Catalyst	
Catalyst Pretreatment	
Reduction temperature (°C)	360
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	8 ( $7.84 \times 10^{-1}$ )
Desulfurization Conditions	
Temperature (°C)	330
Pressure (kg/cm <sup>2</sup> ) (Pressure (MPa))	8 ( $7.84 \times 10^{-1}$ )
LHSV (vol/vol h <sup>-1</sup> )	2
Hydrogen/kerosene (vol/vol)	150
Carbonic acid gas content (vol%)	
Methanation	
Properties of Desulfurized Kerosene	
Sulfur content (wt. ppm)	1
Hydrogen sulfide leakage	present

[0060] The nickel component serves to cause sulfur compounds contained in a kerosene to react with hydrogen (undergo hydrogenation reaction) and thereby convert them into hydrogen sulfide. Consequently, in the case where the content in terms of nickel oxide was lower than a given value as shown in Comparative Example 1, the catalyst had a small NO adsorption and insufficient activity. Because of this, desulfurization was so insufficient that the product had a sulfur content of 0.8 wt. ppm. Conversely, in the case where the content in terms of nickel oxide was too high (35 wt%) as shown in Comparative Example 4, the catalyst had an NO adsorption as small as 3.7 ml/g. This indicates that the nickel component, although contained in a large amount, less contributed to catalytic activity, i.e., had a reduced degree of dispersion. As a result, the sulfur content in the product was 0.2 wt. ppm at the lowest. Thus, the content of the nickel component is preferably in the range of from 5 to 25% by weight in terms of nickel oxide. From the standpoint of hydrogenation activity only, higher nickel component contents are preferred as long as the component is not impaired in dispersion. However, in the present invention, the object is to provide a catalyst excellent in hydrogenation activity and hydrogen sulfide leakage inhibition. Furthermore, since it is inevitable for practical catalysts to be prevented from powdering, the content in terms of nickel oxide is thought to be more preferably from 5 to 20% by weight, most preferably from 10 to 18% by weight, when the effects of the other components are taken in account.

[0061] Zinc oxide has the effect of absorbing the hydrogen sulfide generated by the reaction of sulfur compounds

5 contained in the kerosene with hydrogen (hydrogenation reaction) on the nickel component (active sites). It further has the effect of regulating the oxidized state of the nickel component. Consequently, in the case where the content of the zinc oxide component is low (Comparative Example 3), hydrogen sulfide leaks out to the downstream side. Although a steam reformer or the like is usually disposed on the downstream side, there is a higher possibility that the steam-reforming catalyst might be poisoned by the leakage of hydrogen sulfide and this poisoning arouses troubles in the whole apparatus such as a hydrogen production apparatus. Furthermore, in the case where hydrogen gas containing carbonic acid gas is used for a system containing no zinc oxide, methanation is apt to occur as shown in Comparative Example 8. This is because methanation is apt to proceed on (in) metallic nickel. These results show that the incorporation of zinc oxide is effective in properly maintaining an oxidized state of the nickel component.

10 [0062] Aluminum oxide has the effect of not only increasing the specific surface area to thereby heighten the probability of contact between reactants (kerosene and hydrogen) but also maintaining a strength. Consequently, in the case where aluminum oxide had not been added (Comparative Example 2), the sulfur content in the product was 0.2 wt. ppm at the lowest because of the too small specific surface area. Furthermore, the catalyst which had been subjected to the reaction had cracked, showing that the catalyst was unable to be used over long.

15 [0063] These results show that it is important to enable the nickel component, zinc oxide component, and aluminum oxide component to produce their respective effects while attaining a good balance among these.

[0064] As described above, by using the catalyst of the present invention, a mineral oil corresponding to kerosene can be deeply desulfurized stably.

20 **INDUSTRIAL APPLICABILITY**

[0065] The deep desulfurization catalyst of the present invention has such activity and strength that a mineral oil corresponding to kerosene can be deeply desulfurized to 0.1 wt. ppm or lower under relatively low-pressure conditions even with hydrogen containing carbonic acid gas while inhibiting methanation reaction and preventing oil alteration and that long-term stable operation is possible.

**Claims**

30 1. A catalyst for deep desulfurization of a mineral oil corresponding to kerosene, comprising a nickel component of nickel and nickel oxide, zinc oxide, and aluminum oxide,  
 wherein the content of the nickel component in terms of nickel oxide is from 5 to 25% by weight and the content of the zinc oxide is from 30 to 70% by weight each based on the total of the content of the nickel component in terms of nickel oxide, the content of the zinc oxide, and the content of the aluminum oxide,

35 the nitrogen monoxide adsorption of the catalyst at 1 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> MPa) and 40°C after hydrogen reduction at 360°C is 4.0 ml/g or more in terms of standard-state, and  
 the catalyst has a specific surface area of from 10 to 300 m<sup>2</sup>/g.

40 2. The deep desulfurization catalyst according to claim 1, which is obtained by carrying out an activation treatment in the presence of hydrogen at a temperature of from 200 to 400°C and a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa).

45 3. A process for producing the deep desulfurization catalyst according to claim 1, comprising mixing a basic substance with each of an aqueous solution of a water-soluble nickel metal salt and an aqueous solution of a water-soluble zinc metal salt or with a mixed aqueous solution thereof to thereby form precipitates separately or simultaneously, and mixing the precipitates with aluminum oxide or an aluminum oxide precursor, followed by molding and burning.

50 4. A method of deep desulfurization, comprising bringing a mineral oil corresponding to kerosene into contact with hydrogen in the presence of the deep desulfurization catalyst according to claim 1 or 2 at a temperature of from 200 to 400°C, a pressure of from 1 to 20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup> to 1.96 MPa), and an LHSV of from 0.1 to 5.

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Totoroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Keisai Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JICST FILE (JOIS) : desulfurisation+nickel+zinc+alumina WPI/L (QUESTEL) : Ni and Zn and desulfur? CA(STN) : Al. Ni.O.Zn/MF and desulfur?		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 6-80972, A (Sekiyu Sangyo Kaseika Center, et al.), 22 March, 1994 (22.03.94), Claims; description, Par. Nos. 9 to 12, 18; examples 3, 4, 9, 11 (Family: none)	1-4
Y	US, 4985074, A (Osaka Gas Company Limited), 15 January, 1991 (15.01.91), Claims 2, 8 to 13; description, Column 1, lines 21 to 29; Column 2, line 33 to Column 3, line 53; especially, Column 2, line 63 to Column 3, line 5; examples 4 to 6, 10 to 12 & JP, 1-123628, A Claims; description, page 1, right column, lines 9 to 17; page 2, upper left column, line 5 to lower right column. line 5; example & DK, 615988, A & EP, 324071, A1 & CN, 1035254, A	1-4
A	JP, 45-36227, B1 (Maruzen Petrochemical Company, Limited), 18 November, 1970 (18.11.70), Claims; example 6 (Family: none)	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"B" earlier documents but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" documents published prior to the international filing date but later than the priority date claimed</p>		
<p>Date of the actual completion of the international search 21 November, 2000 (21.11.00)</p> <p>Name and mailing address of the ISA/ Japanese Patent Office</p> <p>Faximile No.</p>		<p>Date of mailing of the international search report 05 December, 2000 (05.12.00)</p> <p>Authorized officer</p> <p>Telephone No.</p>

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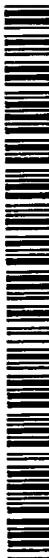
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(54) Title: DEEP DESULFURIZATION CATALYST, METHOD FOR PREPARING THE SAME AND METHOD FOR DESULFURIZATION USING THE SAME

(54) 発明の名称: 深度脱硫触媒、その製造方法及びそれを用いた脱硫方法

WO 01/15804 A1

(57) Abstract: A deep desulfurization catalyst for a mineral oil corresponding to kerosene which comprises nickel and/or nickel oxide, zinc oxide and aluminum oxide, wherein the content of the nickel component in terms of nickel oxide is 5 to 25 wt% and that of zinc oxide is 30 to 70 wt%, both being based on the total amount of all the components, shows, after being hydrogenated at 360°C, an adsorption amount for nitrogen monoxide under 1 kg/cm<sup>2</sup> (9.80 x 10<sup>-2</sup> MPa) at 40°C of 4.0 ml/g or more in terms of the amount under standard conditions, and has a specific surface area of 10 to 300 m<sup>2</sup>/g; a deep desulfurization catalyst according to the above, characterized as being prepared through an activation treatment in the presence of hydrogen at a temperature of 200 to 400°C under a pressure of 1 to 20 kg/cm<sup>2</sup> (9.80 x 10<sup>-2</sup> to 1.96 MPa); a method for preparing the above catalyst which comprises mixing one of a water-soluble nickel metal salt and a water-soluble zinc metal salt or a mixture thereof with a basic material, to form separate precipitates containing nickel or zinc or a precipitate containing nickel and zinc, and then mixing the resultant precipitate with aluminum oxide or an aluminum oxide precursor, followed by molding and firing; and a method for deep desulfurization comprising contacting a mineral oil corresponding to kerosene with hydrogen under conditions of 200 to 400°C, 1 to 20 kg/cm<sup>2</sup> (9.80 x 10<sup>-2</sup> to 1.96 MPa) and a LHSV of 0.1 to 5.

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## (57) 要約:

ニッケル及び／又は酸化ニッケル、酸化亜鉛、酸化アルミニウムからなり、ニッケル成分の含有量を酸化ニッケル含有量で換算して、全成分の合計量に対し、ニッケル成分含有量が5～25重量%、酸化亜鉛含有量が30～70重量%であり、360°Cで水素還元後、 $1\text{kg}/\text{cm}^2(9.80 \times 10^{-3}\text{MPa})$ 、40°Cでの一酸化窒素吸着量が標準状態で4.0ml/g以上であり、比表面積が10～300 $\text{m}^2/\text{g}$ である灯油相当鉱油の深度脱硫触媒；水素存在下、200～400°C、 $1\text{~}20\text{kg}/\text{cm}^2(9.80 \times 10^{-3}\text{~}1.96\text{MPa})$ の範囲内で活性化処理して得られる前記触媒；水溶性ニッケル金属塩及び水溶性亜鉛金属塩の各水溶液又は混合水溶液に、塩基性物質を混合して沈殿物を別個又は同時に生成させ、この沈殿物と酸化アルミニウム又は酸化アルミニウム前駆体を混合、成型及び焼成する前記触媒の製造方法；前記触媒の存在下、灯油相当鉱油と水素を200～400°C、 $1\text{~}20\text{kg}/\text{cm}^2(9.80 \times 10^{-3}\text{~}1.96\text{MPa})$ 、LHSV0.1～5の条件で接触させる深度脱硫方法。

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## 明細書

## 深度脱硫触媒、その製造方法及びそれを用いた脱硫方法

## 技術分野

本発明は、灯油相当鉱油の深度脱硫触媒、その製造方法及びその触媒を用いた深度脱硫方法に関する。特に水蒸気改質反応に共する灯油相当鉱油の前処理行程としての深度脱硫に使用できる深度脱硫触媒、その製造方法及びその触媒を用いた深度脱硫方法に関する。

## 背景技術

水素製造方法には、古くは水の電気分解が知られ、最近では軽質炭化水素の部分酸化、オートサーマルリフューミング (ATR) 等の方法が提案されているが、小型水素製造装置や、燃料電池システムに対し、取り扱い性が優れ、比較的安価な水素製造方法として、水蒸気改質法が適している。

一般に水蒸気改質触媒は硫黄化合物によって被毒されやすいため、原料炭化水素はあらかじめ脱硫（前処理）する事が必要である。従って、これまで、硫黄分の含有量が少ない、もしくは脱硫が容易なナフサより軽質な炭化水素が主として用いられてきた。しかしながら、ナフサ等の炭化水素は一般に広く流通しておらず、小型水素製造設備や燃料電池システムの水素発生設備を所有する小口需要家にとっては流通面での問題を有している。また、揮発性に富むなどの取り扱い性に問題があると言われている。

最近、環境保全の観点から、クリーンなエネルギーに対する期待が高くなり、流通性、取り扱い性、経済性に優れた原燃料からの水素製造技術が待たれている。水蒸気改質触媒は容易に被毒されるため数百 ppb 以下に脱硫することが求められるが、灯油相当の鉱油には芳香族系の硫黄化合物、いわゆる難脱硫性化合物を含むため深度脱硫を行うことは極めて難しい。とりわけ、小型の水素製造設備や燃料電池システムにおいては、装置

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の小型化が不可欠であるため、水素精製ユニットを無くす場合もあり得る。従って、脱硫の際に用いる水素の中に二酸化炭素等が含まれるケースも想定した触媒設計が必要になる。二酸化炭素が存在した場合には、脱硫反応の他に、これらのメタン化反応が進行するため反応熱によって温度制御が困難になるなどの問題が生ずる可能性が高くなる恐れが高くなる。

また、脱硫率を高めた運転条件で従来の触媒を使用して、灯油相当の鉱油を数百 ppb レベルに脱硫できた場合でも、灯油の変質（黄変等）の可能性、触媒の粉化、下流側への硫化水素溢出、反応圧が高い事等の問題を有しており、機器構成の簡略化、長期間安定運転を視野に入れた、さらに高性能な脱硫触媒開発が望まれているのが現状である。

#### 発明の開示

本発明は、比較的低圧条件下で、炭酸ガスを含有する水素を用いてもメタン化反応を抑制し、灯油相当鉱油を変質を起こさずに 0.1 wt. ppm (=100 wt. ppb) 以下に深度脱硫でき、かつ長期間安定運転のできる活性及び強度を有する深度脱硫触媒、その製造方法並びにそれを用いた深度脱硫方法を提供することを目的とする。

本発明は、ニッケル及び酸化ニッケルのニッケル成分、酸化亜鉛及び酸化アルミニウムからなり、ニッケル成分の酸化ニッケル換算含有量と、酸化亜鉛含有量及び酸化アルミニウム含有量の合計量に対し、ニッケル成分の含有量が酸化ニッケル換算で 5~25 重量%、酸化亜鉛の含有量が 30~70 重量%であり、360°Cで水素還元後、常圧、40°Cでの一酸化窒素吸着量が標準状態換算で 4.0 ml/g 以上であり、比表面積が 10~300 m<sup>2</sup>/g であることを特徴とする灯油相当鉱油の深度脱硫触媒に関する。

また、本発明は、水素存在下、温度が 200~400°C、圧力が 1~20 kg/cm<sup>2</sup> (9.80 × 10<sup>-2</sup>~1.96 MPa) の範囲内で活性化処理して得られることを特徴とする上記深度脱硫触媒に関する。

さらに、本発明は、水溶性ニッケル金属塩および水溶性亜鉛金属塩の各水溶液又は混合水溶液に、塩基性物質を混合して沈殿物を別個もしくは同時に生成させ、この沈殿物

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と酸化アルミニウムもしくは酸化アルミニウム前駆体を混合、成型および焼成することにより得られることを特徴とする上記の深度脱硫触媒の製造方法に関する。

さらに、本発明は、上記の深度脱硫触媒の存在下、灯油相当鉛油と水素を温度が 200～400°C、圧力が 1～20 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$ ～1.96 MPa)、LHSV (liquid hourly space velocity) が 0.1～5 の条件で、接触させることを特徴とする深度脱硫方法に関する。

#### 発明を実施するための最良の形態

以下に、本発明を詳細に説明する。

本発明者らは、上記目的を達成するために、鋭意検討を重ねた結果、水溶性ニッケル金属塩および水溶性亜鉛金属塩を原料とし、塩基溶液中にて沈殿させる行程、酸化アルミニウムもしくは酸化アルミニウム前駆体を混合する工程および焼成工程を経て得られる、特定量のニッケルまたは酸化ニッケル、酸化亜鉛、酸化アルミニウムを含有し、360°Cで水素還元後、常圧、40°Cでの一酸化窒素吸着量が特定量であり、特定範囲の比表面積を有する触媒を用いることにより、灯油相当鉛油を硫黄分を 0.1 ppm 以下まで深度脱硫できることを見出し、本発明を完成するに至った。

#### 触媒組成：

本発明の深度脱硫触媒はニッケルおよび酸化ニッケルのニッケル成分と、酸化亜鉛および酸化アルミニウムの 3 成分から構成される。

ニッケル成分の含有量は、ニッケル成分の酸化ニッケル換算含有量と、酸化亜鉛含有量及び酸化アルミニウム含有量の合計量に対し、酸化ニッケル換算で 5～25 重量%の範囲であり、5～20 重量%の範囲が好ましく、10～18 重量%の範囲が特に好ましい。ニッケル成分は、灯油相当鉛油（以下「灯油」と略記）に含まれる硫黄化合物と水素を反応させ硫化水素に変換させる役割を果たすもので、5 重量%以上で好ましい脱硫性能が得られ、また 25 重量%以下でニッケル成分の分散性が上昇し、触媒性能が充分発揮される。

ニッケル成分中のニッケルと酸化ニッケルの存在比は特に限定されない。

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酸化亜鉛の含有量は、ニッケル成分の酸化ニッケル換算含有量と、酸化亜鉛含有量及び酸化アルミニウム含有量の合計量に対し、30～70 重量%の範囲であり、40～70 重量%の範囲が好ましく、50～70 重量%の範囲が特に好ましい。酸化亜鉛は、ニッケルの酸化状態を程良く維持しつつ、発生する硫化水素を捕捉する役割を持っている。従って、30 重量%以上でこれらの性能が充分発揮でき、メタン化が抑制され、硫化水素の溢出が充分抑制される。また、70 重量%以下とすることにより、ニッケル成分および後述のアルミニウム成分が適度な量で存在し、充分な触媒性能が発揮される。

酸化アルミニウムは、比表面積を高め、触媒（活性点）と灯油および水素との接触を円滑にする（触媒有効係数の向上）作用と、強度を維持する作用を持つ。酸化アルミニウムの含有量は、ニッケル成分の酸化ニッケル換算含有量と、酸化亜鉛含有量及び酸化アルミニウム含有量の合計量に対し、5～65 重量%の範囲が好ましく、10～65 重量%の範囲がより好ましく、20～50 重量%の範囲が最も好ましい。5 重量%以上とすることにより、充分な強度や触媒有効係数が得られ、65 重量%以下とすることにより、ニッケル成分や酸化亜鉛が適度な量で存在し、充分な触媒性能が発揮される。

また、本発明の深度脱硫触媒では、触媒 50～500 mg に水素を通気しながら 360°C で 2 時間水素還元した触媒の 40°C における一酸化窒素吸着量が標準状態換算 (standard temperature and pressure: stp) で 4 ml/g 以上であり、4.0～7.0 ml/g が好ましく、5.0～6.7 ml/g が特に好ましい。4 ml/g 以上とすることにより、充分な脱硫活性を得ることができる。一酸化窒素吸着量は脱硫触媒の活性点量を示すものと考えて良い。触媒作用状態が金属状態 (metallic state) であるならば、一酸化炭素をプローブ (probe molecule) に選択するのが理にかなっているが、本発明の触媒のように、酸化状態の特定が困難なものについては、比較的酸化状態の高い活性点に対しても吸着能を有する一酸化窒素をプローブに選択する方が、より実際的である（たとえば、鈴木、吉澤ら、日本エネルギー学会誌、74 卷、806 頁、1995 年）。

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比表面積は、10～300  $\text{m}^2/\text{g}$  の範囲であり、30～250  $\text{m}^2/\text{g}$  の範囲がより好ましく、40～200  $\text{m}^2/\text{g}$  の範囲が最も好ましい。本願の比表面積は、BET 法により測定され、BET 比表面積 (Braunauer-Emmett-Teller specific surface area) として表される。

#### 触媒の調製方法：

触媒調製方法は含浸法、沈殿法、共沈法、混練法など各種方法を採用できるが、本触媒の性能を充分発揮しやすい方法として沈殿法や共沈法が最も好ましい。

好適な触媒の調製方法としては、水溶性ニッケル金属塩および水溶性亜鉛金属塩の各水溶液又は混合水溶液に、塩基性物質を混合して沈殿物を別個もしくは同時に生成させ、この沈殿物と酸化アルミニウムもしくは酸化アルミニウム前駆体を混合、成型および焼成することにより得られることを特徴とする上記の深度脱硫触媒の製造方法が挙げられる。

好適な触媒の調製方法の態様としては、たとえば水溶性亜鉛塩、水溶性ニッケル塩の混合水溶液を調製し、これに塩基性物質としてアルカリ性水を滴下し、得られた沈殿物を充分均一に混合し、これに酸化アルミニウムまたは酸化アルミニウム前駆体を混合し、成型および焼成する方法がある。

また、水溶性亜鉛塩と水溶性ニッケル塩の各水溶液にそれぞれ塩基性物質としてアルカリ性水を滴下し、得られた沈殿物を、充分均一に混合し、これに酸化アルミニウムまたは酸化アルミニウム前駆体を混合し、成型および焼成すればよい。

なお、ニッケル沈殿物、亜鉛沈殿物と同等な組成物が入手可能であればそれらと酸化アルミニウムまたは酸化アルミニウム前駆体を充分混合し、成型および焼成することによっても同等の性能が得られる。

水溶性ニッケル塩としては、硝酸ニッケル、塩化ニッケル、酢酸ニッケルなど、入手容易なものを使用すればよい。水溶性亜鉛塩としては、硝酸亜鉛、硼酸亜鉛、塩化亜鉛、酢酸亜鉛等の無機亜鉛や、有機亜鉛を適宜使用できる。酸化アルミニウムとしては、 $\gamma$ -アルミナが最も好ましく、比表面積は 100～350  $\text{m}^2/\text{g}$  が好ましく、150～300  $\text{m}^2/\text{g}$  がよ

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り好ましく、180～250 m<sup>2</sup>/g が最も好適である。粒子サイズは 100 mesh の篩を通過するものが好ましく、150 mesh の篩を通過するものがより好ましく、180～200 mesh の篩を通過するものが最も取り扱いやすい。

酸化アルミニウム前駆体は、焼成することにより酸化アルミニウムになるものであればよく、具体例としては、例えば、水酸化アルミニウム、アルミニウムイソプロポキシドなどが挙げられる。なお、アルミニウムイソプロポキシドは、エチレングリコール等の溶媒に溶解し、酸もしくは塩基を触媒として、加水分解および重縮合させ、さらに焼成することにより、酸化アルミニウムにすることができる（アルコキシド法）。

酸化アルミニウム前駆体としては、水酸化アルミニウムを好ましく使用できる。粒子サイズは 100 mesh の篩を通過するものが好ましく、150 mesh の篩を通過するものがより好ましく、180～200 mesh の篩を通過するものが最も取り扱いやすい。

成型方法は押し出し成型（extruding）、打錠成型、プレス成形など公知の方法を好ましく選択できる。形状は円柱状、ラシヒリング状、中空状、球状など反応器や操作条件に相応しい形状を選択することが可能である。打錠成型時に、バインダーとしての有機物、無機化合物を添加することが可能である。

塩基性物質としては、アルカリ金属、アルカリ土類金属などの塩化物、硫酸塩、炭酸塩など、アンモニア、有機アミンなどが挙げられ、炭酸アンモニウム、炭酸ナトリウム、炭酸カルシウムなどの塩基性炭酸塩や、アンモニアなどが好ましく、炭酸アンモニウムおよびアンモニアがより好ましく、炭酸アンモニウムおよびアンモニアの併用が特に好ましい。炭酸アンモニウムおよびアンモニアを併用する場合、それらの使用割合は、1：9～9：1 の範囲が好ましく、2：8～8：2 の範囲が特に好ましい。

塩基性物質は、水溶性ニッケル金属塩および水溶性亜鉛金属塩の各水溶液又は混合水溶液にそのまま添加してもよいし、塩基性物質を水溶液にして添加してもよいが、塩基性物質を水溶液にして添加することが好ましい。

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沈殿物は、酸化アルミニウム又は酸化アルミニウム前駆体と混合する前に、乾燥したほうが好ましい。乾燥方法は、特に制限なく、種々の乾燥方法が適用できる。乾燥温度も特に制限ないが、80～140°Cの範囲が好ましい。乾燥時間は1～24時間が好ましい。

焼成温度は、320～520°Cが好ましく、320～400°Cがより好ましく 350～400°Cが最も好ましい。焼成温度を 320°C以上とすることにより、充分な強度が得られ、焼成温度を 520°C以下とすることにより焼結 (sintering) 等の悪影響が少なくなる。焼成時間は、特に制限ないが、通常 0.1～24時間であればよい。

#### 脱硫方法：

本発明の触媒は、固定床 (fixed bed) 反応器に充填し、温度 200～400°C、好ましくは 220～350°C、最も好ましくは 240～330°C、LHSV 0.1～5 vol/vol h<sup>-1</sup>、好ましくは 0.5～4 vol/vol h<sup>-1</sup>、より好ましくは 0.5～3 vol/vol h<sup>-1</sup>、圧力 1～20 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup>～1.96 MPa)、好ましくは 1～15 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup>～1.47 MPa)、より好ましくは 1～10 kg/cm<sup>2</sup> (9.80×10<sup>-2</sup>～9.80×10<sup>-1</sup> MPa) である。水素/灯油の標準状態換算値での容積比は 30～300、好ましくは 40～200、最も好ましくは 50～150 である。

上述の条件で灯油を脱硫することにより、変質を伴わず 0.1 ppm 以下に深度脱硫できる。

なお、水素には炭酸ガスを含有していても灯油相当鉱油を脱硫することができる。炭酸ガスの許容濃度は 30 vol%以下であり、25 vol%以下がより好ましく、15 vol%以下がさらに好ましい。炭酸ガス含有量をこの範囲にすることにより、相対的に水素分圧が低下することがなく高い脱硫率が得られる。

実際に本発明の触媒及び脱硫方法によって得られる深脱灯油は無色透明である。

反応温度を 200°C以上とすることにより、所望の脱硫性能が得られる。また反応温度を 400°C以下とすることにより、灯油の変質、副生成物の生成を抑えることができる。LHSV の下限は特に限定されないが、0.1 vol/vol h<sup>-1</sup> 以上とすることにより、時間あたりの脱硫効率が高くなり経済的な点から好ましく、5 vol/vol h<sup>-1</sup> 以下とすることにより、

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高い脱硫性能が得られる。圧力に関しては、上限は特に限定されないが、建設、製造コストなどから  $20 \text{ kg/cm}^2$  ( $1.96 \text{ MPa}$ ) が実質的な上限である。また  $1 \text{ kg/cm}^2$  ( $9.80 \times 10^{-2} \text{ MPa}$ ) 以上とすることにより水素分圧が低くなることがなく、所望の脱硫性能が発揮できる。水素/灯油容積比を 30 以上とすることにより、時間あたりの通油量が制限されることなく、300 以下とすることにより水素が充分に反応し、機器が小型化することができる。

本発明の触媒は、水素雰囲気下に置かれれば、所定性能を示すが、脱硫処理に先だって還元処理を行うことがより望ましい。あらかじめ還元処理を行うことで、脱硫反応の初期から安定した触媒活性を得ることができる。還元処理を行うことにより、活性が定常域に達するまで時間を短縮することができ好ましい。活性化処理（水素還元処理）条件としては、温度  $200\text{--}400^\circ\text{C}$ 、好ましくは  $300\text{--}400^\circ\text{C}$ 、最も好ましくは  $330\text{--}380^\circ\text{C}$  である。 $200^\circ\text{C}$ 以上とすることにより充分な活性化が行われ、 $380^\circ\text{C}$ 以下とすることにより、触媒の焼結や還元超過によるメタン化の誘発が少なくなり好ましい。圧力は  $1\text{--}20 \text{ kg/cm}^2$  ( $9.80 \times 10^{-2}\text{--}1.96 \text{ MPa}$ )、好ましくは  $1\text{--}15 \text{ kg/cm}^2$  ( $9.80 \times 10^{-2}\text{--}1.47 \text{ MPa}$ )、最も好ましくは  $1\text{--}10 \text{ kg/cm}^2$  ( $9.80 \times 10^{-2}\text{--}9.80 \times 10^{-1} \text{ MPa}$ ) である。通常は、脱硫時と同じ圧力で行えば問題ない。水素通気量は特に限定されず、GHSV (gas hourly space velocity) で  $100\text{--}9000 \text{ vol/vol h}^{-1}$  の範囲で適宜行えばよい。還元時間は触媒量、反応器の形などにより一概には決まらないが、1~24 時間である。

本発明の触媒より深度脱硫できる灯油相当鉱油は、灯油に相当する鉱油であれば特に制限ないが、灯油相当鉱油の性状としては、引火点は  $40^\circ\text{C}$ 以下が好ましく、蒸留性状は 95%留出温度が  $270^\circ\text{C}$ 以下が好ましく、硫黄分は 0.008 重量%以下が好ましく、芳香族分は 20 vol%以下が好ましい。

本発明を実施例により、さらに詳細に述べ、具体的に説明するが、本発明の範囲は実施例によって限定されるものではない。

実施例を示す前に、物性等の機器分析手法をまとめて示す。

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### 一酸化窒素吸着量の測定：

一酸化窒素吸着量の測定には大倉理研社製自動ガス吸着装置（R6015型）を用いた。試料50～500mgを精秤し、これを石英製もしくは硼珪酸ガラス（通称パイレックスガラス）製のU字型試料管に入れ、高純度ヘリウムを通気させて空気をページした後、水素を通気させながら室温から360℃まで、約1時間かけて昇温させた。360℃に到達後2時間水素気流下で保持し、その後再び高純度ヘリウムガスを通気しながら、40℃まで1時間～2時間かけて冷却した。同温度で高純度一酸化窒素（高千穂化学製、Research Grade）の一定量（0.1ml）を試料上に通気させ、未吸着の一酸化窒素量を熱伝導度型検出器（Thermal Conductivity Detector: TCD）で定量し、40℃の吸着量を標準状態(STP)換算して算出した。

### 触媒の比表面積測定：

BET比表面積の測定には、ベルジャパン社製表面積測定装置（Belsorp 28SA）を用いた。試料500～1000mgを精秤し、これを石英製の試料管に充填し、 $10^{-1} \sim 10^{-3}$  mmHg台に減圧しながら室温から300℃まで1時間かけて昇温し、減圧下、同温度で2時間保持して脱気処理を行った。その後、減圧しながら室温まで降温させ、高純度ヘリウムガスで置換し、脱気後の試料重量を精秤した。この後、液化窒素温度（-196℃）で窒素吸着を行い、比表面積を測定した。

### 硫黄分測定：

製品中の硫黄分測定はラネーニッケル法（検出下限値0.1wt.ppm）により、下流側への硫化水素の溢出しの有無の確認には、北川式検知管によった（下限値0.1wt.ppm）。

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## 実施例 1

硝酸ニッケル 6 水和物 5.8 g と酢酸亜鉛 2 水和物 24.3 g を 1200 ml のイオン交換水に溶解させ、この溶液に 10 wt% の炭酸アンモニウムと 15 wt% アンモニア水を加えて、亜鉛およびニッケル化合物の沈殿を得た。この沈殿物を濾過および水洗後、120°C で 12 時間乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 19.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、510°C で 24 時間焼成して酸化ニッケル 5 wt%、酸化亜鉛 30 wt%、酸化アルミニウム 65 wt% の触媒 A を得た。触媒 A の比表面積は 248 m<sup>2</sup>/g、40°C の一酸化窒素吸着量 (STP) 4.0 ml/g だった。触媒 A 10 g を精秤し、温度 400°C、圧力 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa) で 3 時間水素還元し、これに引き続き、温度 400°C、圧力 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa)、LHSV 0.1 vol/vol h<sup>-1</sup> で市販白灯油 (コスモ石油製、JIS 1 号灯油、硫黄分 50 wt.ppm) を通油した。なお水素/灯油比 (vol/vol at STP) は 300 とした。なお、脱硫時には炭酸ガス 15 vol% を含む水素を用いた。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt.ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、また、メタンの発生は殆ど無かった。反応終了後に触媒を取り出した結果ひび割れは認められなかった。

## 実施例 2

酢酸ニッケル 4 水和物 10.0 g と硝酸亜鉛 6 水和物 43.9 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 15 g を添加し、充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、400°C で 24 時間焼成して酸化ニッケル 10 wt%、酸化亜鉛 40 wt%、酸化アルミニウム 50 wt% の触媒 B を得た。触媒 B の比表面積は 225 m<sup>2</sup>/g、40°C の一酸化窒素吸着量 (STP) 4.8 ml/g だった。触媒 B 10 g を精秤し、温度 380°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa) で 3 時間水素還元し、これに引き続き、温度 350°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa)、LHSV 0.5 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 200 とした。なお、脱硫時には炭酸ガス 20 vol% を含む水素

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を用いた。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、また、メタンの発生は殆ど無かった。反応終了後に触媒を取り出した結果ひび割れは認められなかった。

### 実施例 3

硝酸ニッケル 6 水和物 17.5 g と硝酸亜鉛 6 水和物 65.8 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末 11.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、370°Cで 24 時間焼成して酸化ニッケル 15 wt%、酸化亜鉛 60 wt%、酸化アルミニウム 25 wt%の触媒 C を得た。触媒 C の比表面積は 188 m<sup>2</sup>/g、40°Cでの一酸化窒素吸着量 (STP) 5.8 ml/g だった。触媒 C 10 g を精秤し、温度 360°C、圧力 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa) で 3 時間水素還元し、これに引続き、温度 330°C、圧力 8 kg/cm<sup>2</sup> (7.84×10<sup>-1</sup> MPa)、LHSV 2 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 150 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果ひび割れは認められなかった。

### 実施例 4

硝酸ニッケル 6 水和物 21.0 g と硝酸亜鉛 6 水和物 18.0 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物にγ-アルミニウム粉末 6.6 g を添加し、充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、330°Cで 24 時間焼成して酸化ニッケル 18 wt%、酸化亜鉛 60 wt%、酸化アルミニウム 22 wt%の触媒 D を得た。触媒 D の比表面積は 183 m<sup>2</sup>/g、40°Cでの一酸化窒素吸着量 (STP) 6.3 ml/g だった。触媒 D 10 g を精秤し、温度 360°C、

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圧力  $8 \text{ kg/cm}^2$  ( $7.84 \times 10^{-1} \text{ MPa}$ ) で 3 時間水素還元し、これに引続き、温度  $330^\circ\text{C}$ 、圧力  $8 \text{ kg/cm}^2$  ( $7.84 \times 10^{-1} \text{ MPa}$ )、LHSV  $2.5 \text{ vol/vol h}^{-1}$  で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 100 とした。なお、脱硫時には炭酸ガス 25 vol%を含む水素を用いた。反応 500 時間後の深度脱硫灯油性状は、硫黄分  $0.1 \text{ wt. ppm}$  以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、また、メタンの発生は殆ど無かった。反応終了後に触媒を取り出した結果ひび割れは認められなかった。

#### 実施例 5

酢酸ニッケル 4 水和物  $15.0 \text{ g}$  と硝酸亜鉛 6 水和物  $54.8 \text{ g}$  を  $1200 \text{ ml}$  のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末  $16.1 \text{ g}$  を添加し、充分混練後、押出成型器で外形  $1.6 \text{ mm} \phi$  の柱状に成型し、 $350^\circ\text{C}$ で 24 時間焼成して酸化ニッケル  $15 \text{ wt\%}$ 、酸化亜鉛  $50 \text{ wt\%}$ 、酸化アルミニウム  $35 \text{ wt\%}$ の触媒 E を得た。触媒 E の比表面積は  $203 \text{ m}^2/\text{g}$ 、 $40^\circ\text{C}$ での一酸化窒素吸着量 (STP)  $6.1 \text{ ml/g}$  だった。触媒 E  $10 \text{ g}$  を精秤し、温度  $330^\circ\text{C}$ 、圧力  $15 \text{ kg/cm}^2$  ( $1.47 \text{ MPa}$ ) で 3 時間水素還元し、これに引続き、温度  $240^\circ\text{C}$ 、圧力  $15 \text{ kg/cm}^2$  ( $1.47 \text{ MPa}$ )、LHSV  $3.0 \text{ vol/vol h}^{-1}$  で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 100 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分  $0.1 \text{ wt. ppm}$  以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果ひび割れは認められなかった。

#### 実施例 6

酢酸ニッケル 4 水和物  $20.0 \text{ g}$  と酢酸亜鉛 2 水和物  $56.6 \text{ g}$  を  $1200 \text{ ml}$  のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末  $4.6 \text{ g}$  を添加し、充分混練後、押出成型

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器で外形  $1.6 \text{ mm} \phi$  の柱状に成型し、400°Cで 24 時間焼成して酸化ニッケル 20 wt%、酸化亜鉛 70 wt%、酸化アルミニウム 10 wt%の触媒 F を得た。触媒 F の比表面積は 165  $\text{m}^2/\text{g}$ 、40°Cでの一酸化窒素吸着量 (STP) 6.7 ml/g だった。触媒 F 10 g を精秤し、温度 300°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa) で 3 時間水素還元し、これに引続き、温度 220°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa)、LHSV 4.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 40 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果ひび割れは認められなかった。

#### 実施例 7

酢酸ニッケル 4 水和物 24.9 g と酢酸亜鉛 2 水和物 56.6 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 1.5 g を添加し、充分混練後、押出成型器で外形  $1.6 \text{ mm} \phi$  の柱状に成型し、400°Cで 24 時間焼成して酸化ニッケル 25 wt%、酸化亜鉛 70 wt%、酸化アルミニウム 5 wt%の触媒 G を得た。触媒 G の比表面積は 158  $\text{m}^2/\text{g}$ 、40°Cでの一酸化窒素吸着量 (STP) 6.9 ml/g だった。触媒 G 10 g を精秤し、温度 200°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa) で 3 時間水素還元し、これに引続き、温度 200°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa)、LHSV 5.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 50 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果ひび割れは認められなかった。

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表 1

実施例	1	2	3	4	5	6	7
触媒組成							
酸化ニッケル換算量 (wt%)	5	10	15	18	15	20	25
酸化亜鉛 (wt%)	30	40	60	60	50	70	70
酸化アルミニウム (wt%)	65	50	25	22	35	10	5
触媒の前処理							
還元温度 (°C)	400	380	360	360	330	300	200
圧力 (kg/cm <sup>2</sup> )	1	10	8	8	15	20	20
(圧力 (MPa))	(9.80×10 <sup>-2</sup> )	(9.80×10 <sup>-1</sup> )	(7.80×10 <sup>-1</sup> )	(7.80×10 <sup>-1</sup> )	(1.47)	(1.96)	(1.96)
脱硫条件:							
温度 (°C)	400	350	330	330	240	220	200
圧力 (kg/cm <sup>2</sup> )	1	10	8	8	15	20	20
(圧力 (MPa))	(9.80×10 <sup>-2</sup> )	(9.80×10 <sup>-1</sup> )	(7.80×10 <sup>-1</sup> )	(7.80×10 <sup>-1</sup> )	(1.47)	(1.96)	(1.96)
LHSV (vol/vol h <sup>-1</sup> )	0.1	0.5	2	2.5	3	4	5
水素/灯油 (vol/vol)	300	200	150	100	100	40	50
炭酸ガス含有量 (vol%)	15	20	0	25	0	0	0
メタン化の有無	なし	—	なし	—	—	—	—
触媒物性							
比表面積 (m <sup>2</sup> /g)	248	225	188	183	203	165	158
NO吸着量 (ml/g (sup) at 40°C)	4	4.8	5.8	6.3	6.1	6.7	6.9
反応後の触媒のフレ	なし	なし	なし	なし	なし	なし	なし
脱硫後の灯油性状							
硫黄分 (wt. ppm)	0.1以下	0.1以下	0.1以下	0.1以下	0.1以下	0.1以下	0.1以下
硫化水素の溢出	なし	なし	なし	なし	なし	なし	なし
深度脱硫灯油の呈色	無色透明	無色透明	無色透明	無色透明	無色透明	無色透明	無色透明

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### 比較例 1

硝酸ニッケル 6 水和物 3.5 g と酢酸亜鉛 2 水和物 56.6 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に、10 wt% の炭酸アンモニウムと 15 wt% アンモニア水を加えて、亜鉛およびニッケル化合物の沈殿を得た。この沈殿物を濾過および水洗後、120°C で 12 時間乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 8.1 g を添加し、充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、510°C で 24 時間焼成して酸化ニッケル 3 wt%、酸化亜鉛 70 wt%、酸化アルミニウム 27 wt% の触媒 a を得た。触媒 a の比表面積は 191 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 3.3 ml/g だった。触媒 a 10 g を精秤し、温度 400°C、圧力 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa) で 3 時間水素還元し、これに引き続き、温度 400°C、圧力 1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa)、LHSV 0.1 vol/vol h<sup>-1</sup> で市販白灯油 (コスモ石油製、硫黄分 50 wt. ppm) を通油した。なお水素/灯油比 (vol/vol at STP) は 300 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.8 wt. ppm、また深度脱硫灯油は無色透明であった。脱硫反応中に下流側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果ひび割れは認められなかった。

### 比較例 2

酢酸ニッケル 4 水和物 20 g と硝酸亜鉛 6 水和物 87.7 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。これを充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、400°C で 24 時間焼成して酸化ニッケル 20 wt%、酸化亜鉛 80 wt% の触媒 b を得た。触媒 b の比表面積は 10 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 3.8 ml/g だった。触媒 b 10 g を精秤し、温度 380°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa) で 3 時間水素還元し、これに引き続き、温度 350°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa)、LHSV 0.5 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 200 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.2 wt. ppm 以下、また深度脱硫灯油は無色透明であった。脱硫反応中に下流

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側への硫化水素の溢出は認められず、反応終了後に触媒を取り出した結果、ひび割れと若干の粉化が認められた。

### 比較例 3

硝酸ニッケル 6 水和物 17.5 g と硝酸亜鉛 6 水和物 27.4 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末 27.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、370°C で 24 時間焼成して酸化ニッケル 15 wt%、酸化亜鉛 25 wt%、酸化アルミニウム 60 wt% の触媒 c を得た。触媒 c の比表面積は 240 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 4.5 ml/g だった。触媒 c 10 g を精秤し、温度 360°C、圧力 8 kg/cm<sup>2</sup> (7.84 × 10<sup>-1</sup> MPa) で 3 時間水素還元し、これに引き続き、温度 330°C、圧力 8 kg/cm<sup>2</sup> (7.84 × 10<sup>-1</sup> MPa)、LHSV 2.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 150 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。しかし、脱硫反応中に下流側への硫化水素の溢出が認められた。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

### 比較例 4

硝酸ニッケル 6 水和物 40.9 g と酢酸亜鉛 2 水和 40.5 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末 27.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、370°C で 24 時間焼成して酸化ニッケル 35 wt%、酸化亜鉛 50 wt%、酸化アルミニウム 15 wt% の触媒 d 得た。触媒 d の比表面積は 173 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 3.7 ml/g だった。触媒 d 10 g を精秤し、温度 330°C、圧力 15 kg/cm<sup>2</sup> (1.47 MPa) で 3 時間水素還元し、これに引き続き、温度 240°C、圧力 15 kg/cm<sup>2</sup> (1.47 MPa)、LHSV 3.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比

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(vol/vol at STP) は 100 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.2 wt. ppm、また深度脱硫灯油は無色透明であった。また、脱硫反応中に下流側への硫化水素の溢出は認められなかった。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

#### 比較例 5

酢酸ニッケル 4 水和物 5.0 g と硝酸亜鉛 6 水和物 21.9 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 22.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、400°C で 24 時間焼成して酸化ニッケル 5 wt%、酸化亜鉛 20 wt%、酸化アルミニウム 75 wt% の触媒 e 得た。触媒 e の比表面積は 263 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 5.0 ml/g だった。触媒 e 10 g を精秤し、温度 300°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa) で 3 時間水素還元し、これに引き続き、温度 220°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa)、LHSV 4.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 50 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は無色透明であった。しかし、脱硫反応中に下流側への硫化水素の溢出が認められた。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

#### 比較例 6

硝酸ニッケル 6 水和物 17.5 g と硝酸亜鉛 6 水和物 27.4 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に  $\gamma$ -アルミナ粉末 18.0 g を添加し、充分混練後、押出成型器で外形 1.6 mm  $\phi$  の柱状に成型し、370°C で 24 時間焼成して酸化ニッケル 15 wt%、酸化亜鉛 25 wt%、酸化アルミニウム 60 wt% の触媒 f 得た。触媒 f の比表面積は 240 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 5.8 ml/g だった。触媒 f 10 g を精秤し、温度 360°C、圧力 20 kg/cm<sup>2</sup> (1.96 MPa) で 3 時間水素還元し、これに引き続き、温度 480°C、圧力 8

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kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa)、LHSV 2.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 150 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.1 wt. ppm 以下、また深度脱硫灯油は黄変した。脱硫反応中に下流側への硫化水素の溢出が認められなかった。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

#### 比較例 7

酢酸ニッケル 4 水和物 15.0 g と硝酸亜鉛 6 水和物 27.4 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様に亜鉛およびニッケル化合物の沈殿を得たあと、乾燥させた。得られた沈殿物に水酸化アルミニウム粉末 27.5 g を添加し、充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、370°C で 24 時間焼成して酸化ニッケル 15 wt%、酸化亜鉛 25 wt%、酸化アルミニウム 60 wt% の触媒 g 得た。触媒 g の比表面積は 240 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 5.8 ml/g だった。触媒 g 10 g を精秤し、温度 360°C、圧力 20 kg/cm<sup>2</sup> ( $1.96$  MPa) で 3 時間水素還元し、これに引き続き、温度 150°C、圧力 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa)、LHSV 2.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 150 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.6 wt. ppm、深度脱硫灯油は無色透明だった。脱硫反応中に下流側への硫化水素の溢出が認められなかった。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

#### 比較例 8

酢酸ニッケル 4 水和物 20 g を 1200 ml のイオン交換水に溶解させ、実施例 1 と同様にニッケル化合物の沈殿を得た後、乾燥させた。得られた沈殿物に酸化アルミニウム粉末 24 g を添加し、これを充分混練後、押出成型器で外形 1.6 mm φ の柱状に成型し、400°C で 24 時間焼成して酸化ニッケル 20 wt%、酸化アルミニウム 80 wt% の触媒 h 得た。触媒 h の比表面積は 270 m<sup>2</sup>/g、40°C での一酸化窒素吸着量 (STP) 5.9 ml/g だった。触媒 h

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10 g を精秤し、温度 380°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa) で 3 時間水素還元し、これに引き続き、温度 350°C、圧力 10 kg/cm<sup>2</sup> ( $9.80 \times 10^{-1}$  MPa)、LHSV 0.5 vol/vol h<sup>-1</sup> で市販白灯油を通油した。なお水素/灯油比 (vol/vol at STP) は 200 とした。脱硫時には炭酸ガス 25 vol%を含む水素を用いた。反応 500 時間後の深度脱硫灯油性状は、硫黄分 0.9 wt. ppm、深度脱硫灯油は無色透明だった。脱硫反応中に下流側への硫化水素の溢出が認められた。また、メタンの発生も認められた。反応終了後に触媒を取り出した結果、ひび割れは認められなかった。

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表2

比較例		1	2	3	4	5	6	7	8
触媒組成									
酸化ニッケル換算量 (wt%)	3	20	15	35	5	15	15	20	
酸化亜鉛 (wt%)	70	80	25	50	20	25	25	0	
酸化アルミニウム (wt%)	27	0	60	15	75	60	60	80	
触媒の前処理									
還元温度 (°C)	400	380	360	330	300	360	360	380	
圧力 (kg/cm <sup>2</sup> )	1	10	8	15	20	20	20	10	
(圧力 (MPa))	(9.80×10 <sup>-3</sup> )	(9.80×10 <sup>-1</sup> )	(7.84×10 <sup>-1</sup> )	(1.47)	(1.96)	(1.96)	(1.96)	(9.80×10 <sup>-1</sup> )	
脱硫条件									
温度 (°C)	400	350	330	240	220	480	150	350	
圧力 (kg/cm <sup>2</sup> )	1	10	8	15	20	8	8	10	
(圧力 (MPa))	(9.80×10 <sup>-3</sup> )	(9.80×10 <sup>-1</sup> )	(7.84×10 <sup>-1</sup> )	(1.47)	(1.96)	(7.84×10 <sup>-1</sup> )	(7.84×10 <sup>-1</sup> )	(9.80×10 <sup>-1</sup> )	
LHSV (vol/vol h <sup>-1</sup> )	0.1	0.5	2	3	4	2	2	0.5	
水素/灯油 (vol/vol)	300	200	150	100	50	150	150	200	
炭酸ガス含有量 (vol%)									
メタン化の有無	なし							あり	
触媒物性									
比表面積 (m <sup>2</sup> /g)									
NO吸着量 (ml/g (stp)) at 40°C	191	10	240	173	263	240	240	270	
反応後の触媒のワレ	3.3	3.8	4.5	3.7	5	5.8	5.8	5.8	
なし	あり	なし	なし	なし	なし	なし	なし	なし	
脱硫後の灯油性状									
硫黄分 (wt. ppm)	0.8	0.2	0.1以下	0.2	0.1以下	0.1以下	0.6	0.9	
硫化水素の溢出	なし	なし	あり	なし	なし	なし	なし	あり	
深度脱硫灯油の呈色	無色透明	無色透明	無色透明	無色透明	無色透明	無色透明	無色透明	無色透明	

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## 参考例 1

市販脱硫触媒 10 ml を温度 360°C、圧力 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa) で 3 時間水素還元し、これに引き続き、温度 330°C、圧力 8 kg/cm<sup>2</sup> ( $7.84 \times 10^{-1}$  MPa)、LHSV 2.0 vol/vol h<sup>-1</sup> で市販白灯油を通油した。この時の水素/灯油比 (vol/vol at STP) は 150 とした。反応 500 時間後の深度脱硫灯油性状は、硫黄分 1 wt. ppm、深度脱硫灯油は黄変した。また脱硫反応中に下流側への硫化水素の溢出が認められた。

表 3

参考例	1
<b>市販触媒</b>	
触媒の前処理	
還元温度 (°C)	360
圧力 (kg/cm <sup>2</sup> )	8
(圧力 (MPa))	( $7.84 \times 10^{-1}$ )
<b>脱硫条件</b>	
温度 (°C)	330
圧力 (kg/cm <sup>2</sup> )	8
(圧力 (MPa))	( $7.84 \times 10^{-1}$ )
LHSV (vol/vol h <sup>-1</sup> )	2
水素/灯油 (vol/vol)	150
炭酸ガス含有量 (vol%)	
メタン化の有無	
<b>脱硫後の灯油性状</b>	
硫黄分 (wt. ppm)	1
硫化水素の溢出	あり

ニッケル成分は灯油に含まれる硫黄化合物を水素と反応（水素化反応）させ硫化水素に変換させる役割を持つ。従って比較例 1 に示すように酸化ニッケル換算含有量が規定値以下の場合には、NO 吸着量も少なく、触媒の活性が不充分であるために製品中の硫黄分は 0.8 wt. ppm までしか脱硫できなかった。逆に、比較例 4 に示すように、酸化ニッケル換算含有量が多すぎる場合 (35 wt%) の NO 吸着量は 3.7 ml/g と少なく、ニッケル成分が多く含まれていても触媒活性に関与する割合が低い、すなわち分散性が低下してい

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ることを示している。その結果、製品中の硫黄分は 0.2 wt. ppm にとどまった。このようにニッケル成分は酸化ニッケル換算で 5~25 重量%の範囲が好ましい。水素化活性だけの観点からすれば分散性を損ねない範囲で、ニッケル成分の含有量は高いほど好ましいことになるが、本発明では水素化活性、硫化水素溢出抑制に優れる触媒の提供が目的である。また、実用触媒には粉化防止対策は不可避であるため、他成分の効果を勘案し、酸化ニッケル換算含有量は 5~20 重量%がより好ましく、10~18 重量%の範囲が最も好適であると考えられる。

酸化亜鉛にはニッケル成分（活性点）上で、灯油中の硫黄化合物と水素が反応（水素化反応）して生じた硫化水素を吸收させる効果がある。これと同時にニッケル成分の酸化状態を制御する効果を有する。従って、酸化亜鉛成分が少ない場合（比較例 3）では、下流側に硫化水素が溢出する。通常下流側には水蒸気改質器等が設置されるが、硫化水素の溢出によって水蒸気改質触媒が被毒される可能性が高まり、水素製造設備などの装置全体に不具合が生じる。また、酸化亜鉛を全く含まない系に炭酸ガス含有水素ガスを用いた場合には、比較例 8 に示すように、メタン化が起こりやすくなる。メタン化は金属状態のニッケル（in）上で進行し易いためで、酸化亜鉛を含有させることでニッケル成分の酸化状態を程良く保っていることが分かる。

酸化アルミニウムには、比表面積を高め反応物質（灯油と水素）の接触確率を高めるとともに、強度を維持させる効果がある。従って酸化アルミニウムを添加しない場合（比較例 2）では比表面積が低すぎるために、製品中の硫黄分は 0.2 wt. ppm に留まった。また、反応に供した触媒にはひび割れは認められ、長期に渡って使用することは出来ないことが分かる。

これらの結果が示すように、ニッケル成分、酸化亜鉛成分および酸化アルミニウム各成分の持つ効果をバランス良く発揮させることが重要である。

このように、本発明による触媒を用いることで、灯油相当鉻油を安定して深度脱硫することができる。

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### 産業上の利用可能性

本発明の深度脱硫触媒は、比較的低圧条件下で、炭酸ガスを含有する水素を用いてもメタン化反応を抑制し、灯油相当鉱油を変質を起こさずに 0.1 wt. ppm 以下に深度脱硫でき、かつ長期間安定運転のできる活性及び強度を有する。

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## 請 求 の 範 囲

1. ニッケル及び酸化ニッケルのニッケル成分、酸化亜鉛及び酸化アルミニウムからなり、ニッケル成分の酸化ニッケル換算含有量と、酸化亜鉛含有量及び酸化アルミニウム含有量の合計量に対し、ニッケル成分の含有量が酸化ニッケル換算で 5~25 重量%、酸化亜鉛の含有量が 30~70 重量%であり、360°Cで水素還元後、1 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$  MPa)、40°Cでの一酸化窒素吸着量が標準状態換算で 4.0 ml/g 以上であり、比表面積が 10~300 m<sup>2</sup>/g であることを特徴とする灯油相当鉱油の深度脱硫触媒。
2. 水素存在下、温度が 200~400°C、圧力が 1~20 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$ ~1.96 MPa) の範囲内で活性化処理して得られることを特徴とする請求の範囲 1 に記載の深度脱硫触媒。
3. 水溶性ニッケル金属塩および水溶性亜鉛金属塩の各水溶液又は混合水溶液に、塩基性物質を混合して沈殿物を別個もしくは同時に生成させ、この沈殿物と酸化アルミニウムもしくは酸化アルミニウム前駆体を混合、成型および焼成することにより得られることを特徴とする請求の範囲 1 に記載の深度脱硫触媒の製造方法。
4. 請求の範囲 1 又は 2 に記載の深度脱硫触媒の存在下、灯油相当鉱油と水素を温度が 200~400°C、圧力が 1~20 kg/cm<sup>2</sup> ( $9.80 \times 10^{-2}$ ~1.96 MPa)、LHSV が 0.1~5 の条件で、接触させることを特徴とする深度脱硫方法。

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/05708

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl' B01J 23/80, C10G 45/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl' B01J 21/00-38/74, C10G 1/00-75/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2000
Kokai Jitsuyo Shinan Koho	1971-2000	Jitsuyo Shinan Keisai Koho	1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JICST FILE (JOIS) : desulfurisation\*nickel\*zinc\*alumina  
 WPI/L(QUESTEL) : Ni and Zn and desulfur?  
 CA(STN) : Al.Ni.O.Zn/MF and desulfur?

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 6-80972, A (Sekiyu Sangyo Kasseika Center, et al.), 22 March, 1994 (22.03.94), Claims; description, Par. Nos. 9 to 12, 18; examples 3, 4, 9, 11 (Family: none)	1-4
Y	US, 4985074, A (Osaka Gas Company Limited), 15 January, 1991 (15.01.91), Claims 2, 8 to 13; description, Column 1, lines 21 to 29; Column 2, line 33 to Column 3, line 53; especially, Column 2, line 63 to Column 3, line 5; examples 4 to 6, 10 to 12 & JP, 1-123628, A Claims; description, page 1, right column, lines 9 to 17; page 2, upper left column, line 5 to lower right column, line 5; example & DK, 615988, A & EP, 324071, A1 & CN, 1035254, A	1-4
A	JP, 45-36227, B1 (Maruzen Petrochemical Company, Limited), 18 November, 1970 (18.11.70), Claims; example 6 (Family: none)	1-4

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 November, 2000 (21.11.00)	Date of mailing of the international search report 05 December, 2000 (05.12.00)
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Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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## A. 発明の属する分野の分類 (国際特許分類 (IPC))

Int.Cl. 7 B01J 23/80, C10G 45/06

## B. 調査を行った分野

調査を行った最小限資料 (国際特許分類 (IPC))

Int.Cl. 7 B01J 21/00-38/74, C10G 1/00-75/04

## 最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	1926-1996年
日本国公開実用新案公報	1971-2000年
日本国登録実用新案公報	1994-2000年
日本国実用新案掲載公報	1996-2000年

国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

JICSTファイル(JOIS) : 脱硫\*ニッケル\*亜鉛\*アルミナ

WPI/L(QUESTEL) : Ni and Zn and desulfur?

CA(STN) : Al. Ni. O. Zn/MF and desulfur?

## C. 関連すると認められる文献

引用文献の カテゴリーエ	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
Y	JP, 6-80972, A(財団法人石油産業活性化センター、外1名)22.3 月.1994(22.03.94), 特許請求の範囲, 明細書第9~12段落, 第18 段落, 実施例3, 4, 9, 11(ファミリーなし)	1-4
Y	US, 4985074, A(Osaka Gas Company Limited)15.1月.1991(1 5.01.91), 特許請求の範囲第2, 8-13項, 明細書第1欄第21-29 行, 第2欄第33行-第3欄53行, 特に, 第2欄第63行-第3欄第5行, 実施例4-6, 10-12&JP, 1-123628, A; 特許請求の範囲, 明細書 第1頁右欄第9-17行, 第2頁左上欄第5行-右下欄第5行, 実施例& DK, 615988, A&EP, 324071, A1&CN, 1035254, A	1-4

 C欄の続きにも文献が列挙されている。 パテントファミリーに関する別紙を参照。

## \* 引用文献のカテゴリ

「A」特に関連のある文献ではなく、一般的技術水準を示す  
もの「E」国際出願日前の出願または特許であるが、国際出願日  
以後に公表されたもの「L」優先権主張に疑義を提起する文献又は他の文献の発行  
日若しくは他の特別な理由を確立するために引用する  
文献 (理由を付す)

「O」口頭による開示、使用、展示等に言及する文献

「P」国際出願日前で、かつ優先権の主張の基礎となる出願

## の日の後に公表された文献

「T」国際出願日又は優先日後に公表された文献であって  
出願と矛盾するものではなく、発明の原理又は理論  
の理解のために引用するもの「X」特に関連のある文献であって、当該文献のみで発明  
の新規性又は進歩性がないと考えられるもの「Y」特に関連のある文献であって、当該文献と他の1以  
上の文献との、当業者にとって自明である組合せに  
よって進歩性がないと考えられるもの

「&amp;」同一パテントファミリー文献

## 国際調査を完了した日

21. 11. 00

## 国際調査報告の発送日

05.12.00

## 国際調査機関の名称及びあて先

日本国特許庁 (ISA/JP)

郵便番号 100-8915

東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)

関 美 祐

4 G 9045

(8月)

電話番号 03-3581-1101 内線 3416

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## C (続き) 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	JP, 45-36227, B1(丸善石油株式会社)18.11月.1970(18.11.70), 特許請求の範囲, 実施例6(ファミリーなし)	1-4

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